C Unit 5 C{PRIVATE }

Sampling and Data Interpretation

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C **Unit 5** C{PRIVATE }

Sampling and Data Interpretation

Sampling is an integral part of most scientific investigations, and investigations involving hazardous materials are no exception. Sampling (and subsequent analysis) is the basic means of determining if a site is contaminated. Sampling identifies the contaminants, indicates how well cleanup efforts are achieving their intended goal, and determines when remediation is complete.

Sampling collects a small, representative portion of a substance. Sample size is dependent on the quantity needed for analysis. Representativeness of the sample is critical; the sample must accurately reflect the nature of the substance under investigation. If a sampling program is designed to collect samples from the same location over a period of time to determine change, this sampling process is called monitoring.

This unit summarizes the basic techniques of sampling hazardous substances and the interpretation of the resultant laboratory data. More details on this involved and often complex process can be found in the literature listed at the end of this unit.

5.1 BASIC CONSIDERATIONS PRIOR TO SAMPLING

Before collecting samples, a substantial amount of work must be done to organize all the details of the sampling program. Once in the field, the sampling process should read like a cookbook; all procedures are listed in a simple, sequential format.

Extreme caution should be used when sampling, especially drums and containers, since accidents frequently occur when sampling drums and containers. Prior to sampling, all personnel should be adequately trained and warned of the hazards of the materials being sampled. In addition to proper sampling techniques, personnel should also be trained in identifying hazards, how to minimize hazards and to be alert for any new potential hazards which may occur during sampling. Sampling, especially containers and drums, is DANGEROUS BUSINESS!

5.1.1 SAMPLING OBJECTIVES

Well-defined investigative objectives must be prepared prior to sampling. When preparing objectives, items often considered are:

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- site characterization data;
- applicable regulations;
- nature and extent of suspected contamination;
- contaminant source characterization;
- potential receptors (soil, sediment, surface water, ground water, plants, animals, man, etc.); and
- worker health and safety.

The first stage in identifying the overall project objectives is essentially a preliminary planning stage in which the general investigative objectives are identified. This is followed by identifying the specific data quality objectives (DQOs). The DQOs identify necessary sampling objectives and the required level of data quality. Once this is clearly identified, then a sampling and analysis plan can be formulated.

5.1.2 SAMPLING DESIGN

Sampling design, or the selection of sampling locations, is critical to the success of the investigative program. Sampling design will determine the extent of sampling, how the data can be statistically analyzed, what conclusions can be supported from the data, and how well the data will hold up in court.

Four basic sample designs are commonly used in hazardous waste investigations: judgmental, random, systematic, and combination. Common terminology has yet to be accepted for the different types of sample design; thus, terms such as "geostatistical" sampling may be used for sampling designs other than random.

5.1.2.1 Judgmental Sampling

This sampling design is used when specific information is known about the configuration of the release. Examples are as follows:

- collecting surface soil samples from a discolored area adjacent to a leaking tank;
- collecting air samples downwind of a release; and
- collecting ground water samples down gradient from a leaking underground tank.

Obviously, this sampling design produces a bias toward the worst contamination, or a "worst case scenario". Additionally, areas of significant contamination can be missed. Sampling locations are selected on the basis where the scientist thinks the contamination should be, considering site characteristics and visual observations. Such judgments are often wrong. Judgmental sampling cannot be analyzed statistically, thus severely limiting data manipulation.

However, this type of sampling is efficient and economical, both in terms of sampling time and laboratory costs. It is probably the most common type of hazardous substance sampling, and is often used during initial investigations.

5.1.2.2 Random Sampling

In random sampling, every portion of the area under investigation has an equal chance of being selected for sample collection. For example, a researcher wants to know the average weight of apples from a particular tree. All the apples are picked, mixed thoroughly in a basket, and a blindfolded sampler picks out a certain number of apples. These apples are then weighed and the average weight calculated. The sample collected and the resulting data are free of bias.

Examples of cases where random sampling might be used include:

- ! an area where there is widespread contamination, especially if there are no visual signs of the contamination;
- ! investigations where the statistical analysis of the data is required; and
- ! investigations where the data collected will be used to support legal decisions.

Statistics are based on the assumption that numerical data was collected at random. Strictly speaking, the use of statistics for data collected using any other sampling design is invalid. However, this view is theoretical in nature and in practice, minor departures from strict randomness are allowed as long as the deviation does not introduce or allow any bias.

A random sampling design does not guarantee good coverage of the sampling area; all samples could be clustered in one corner. The only alternative in this case is to increase the sample size, a time consuming and costly option. A random design precludes investigation of areas where professional judgment suggests some significant spatial event worthy of sampling. In addition, sample locations may fall in areas that cannot be sampled. For example, when collecting soil samples, a random design could locate samples on tops of drums, in paved areas, and other locations where no soil exists. Finally, locating the sampling site in the field may be difficult and time consuming because the locations must be absolutely bias free.

Because of the time and cost involved in a random sampling design

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and the possibility of poor coverage, other sampling schemes are generally used when releases of hazardous substances are investigated.

5.1.2.3 Systematic Sampling

A grid is placed over a map of the study area or a grid is surveyed on the ground. The intersection of grid lines defines where a particular sample is to be collected. This sampling design is used in a variety of situations, such as defining the extent of soil contamination from a leaking underground storage tank. In such cases, statistics are not used to evaluate the data.

The grid area is selected based on sampling needs; thus, locating soil sampling points in a paved area (or other impossible locations) are eliminated. The shape of the grid may be square, rectangular, triangular, or radial, depending on the needs of the investigation. Spacing of the grid is based on the nature of the contamination. If the contamination is expected to be homogeneous, wide spacing may be appropriate because little variation is expected among the samples. In contrast, a heterogeneous area will require small spacing for adequate characterization.

The advantage to systemic sampling is that all portions of the study site are sampled. In addition, impossible locations are avoided, and sampling and laboratory costs are not as high as in random sampling. Bias is limited to selection of study area to be included in the sampling grid, shape of the grid, and spacing of the grid.

The prime disadvantage to systematic sampling is that it involves some judgment that could be challenged by regulators, other investigators, and attorneys. While statistics are occasionally used to evaluated data collected by systematic means, such use of statistics can, and often is, challenged.

5.1.2.4 Combination Sampling Design (Randomized Grid)

This design endeavors to combine the advantages of both random and systematic sampling while avoiding most of the disadvantages. It allows some professional judgement to enter the decision of where to sample, but judgement is limited and significant bias is not introduced. This is probably the most common sampling design for field investigations and is applicable to almost any situation, including

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hazardous waste investigations.

There are numerous ways random and systematic sampling can be combined. One technique is to place a grid over the area and randomly select sampling points within the boundaries of each set of grid lines.

A properly designed randomized grid can eliminate most of the problems associated with either design. Although the "complete randomness" basis of statistics is not strictly followed, the magnitude of deviation is usually not significant. Samples collected in this manner can be successfully defended in court, but complete documentation of all decisions made in designing the sampling plan must be prepared and justified.

5.1.3 TYPES OF SAMPLES

There are three basic types of samples: grab, composite, and integrated. The type of sample collected is determined by sampling objectives and the nature of the material being sampled.

5.1.3.1 Grab Sample

A grab sample is an individual sample taken at a specific location and at a specific time. For example, a single soil sample from the area of a leaky drum for determination if the soil material is a characteristic hazardous waste is a grab sample. The use of the word "grab" is unfortunate, for it can imply that a handful of material is pulled from any convenient point. Grab samples must be collected according to the sampling plan that considers size, shape, location, representativeness, etc. of the sample.

5.1.3.2 Composite Sample

A composite sample is one that is made up of individual samples taken at different locations and mixed together. This mixing of samples from different locations is conducted to give a representative sample or to obtain sufficient material for laboratory analysis. For example, various strata in a drum of hazardous waste may be combined into a composite sample. In effect that is what a CULIWASA (composite liquid waste sampler) sampler accomplishes.

Compositing may be useful in determining the overall extent of a contaminated area, but should not be used as a substitute for characterization of individual constituent concentrations. Composite samples are of limited value because they do not reflect actual concentrations and can reduce some concentrations to below the detection limit. Therefore, compositing should be limited and should always be done in conjunction with an adequate number of grab

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samples.

5.1.3.3 Integrated Sample

An integrated sample is a single sample collected over a period of time. This sampling method is necessary when the material being sampled changes over time or space. For example, the composition and volume of a liquid waste from a processing stream changes with variations in the process itself. Collecting a representative sample may necessitate sampling over a 24 hour period and increasing the sampling frequency during periods of high flow, thus integrating the sample over time and flow volume.

5.1.4 REPRESENTATIVE SAMPLES

Regardless of the sample type, all samples must accurately depict the substance being collected. A more formalized statistical definition of representativeness is as follows: the degree to which the data accurately and precisely represent a characteristic of a population parameter, variation of a property, a process characteristic, or an operational condition.

5.1.5 SAMPLING PLAN

Prior to a sampling effort, a written sampling plan should be prepared. The sampling plan should be integrated with analytical considerations so the document specifies the required analytical procedures and data quality levels. The importance of this relates to proper sample collection, preservation, and timely shipping; and to on-site analytical procedural requirements. The study objectives must be adequately considered with input from regulators, managers, samplers, chemists, etc., sot the DQOs can be achieved and/or revised as necessary. Following are some of the items that should be included in a sampling plan:

- objectives (including DQOs);
- applicable regulations;
- site background information;
- suspected level of contamination;
- training of sampling team;
- sampling/field analysis methods (SOPs);
- justification of selected methods and procedures;
- organization of the investigative team;
- transportation & shipping information (e.g. chain of

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custody, shipping method);
- field notes;
- safety plan (e.g. decontamination; work zones);
- field notes;
- safety plan (e.g. decontamination; work zones);
- quality assurance/quality control;
- chain of custody;
- shipping;
- lab analytical protocol (parameters, methods, detection limits);
- interfacing with laboratory; and
- safety plan.

The standard operating procedures (SOPs) provide the recipe for performing a specific sampling or measurement operation. It includes items such as the instrumental calibration procedure, the required sampling equipment and proper use, sampling containers, sample preservation, etc.

Deviations from the sampling plan and SOPs should be rare and approved by the sampling director. field sampling is not a place where extemporaneous changes, improvisation, or substitution are appropriate. However, unanticipated field conditions can lead to inappropriate specifications in the sampling plan. It is imperative that the field investigative team possesses sufficient knowledge so problems in the field can be identified and appropriately handled. Any deviations from the sampling protocol must be fully documented and justified.

5.2 SAMPLING EQUIPMENT

Regardless of the media to be sampled, equipment selection must consider the following items.

- **Safety**. The equipment selected must minimize both chemical and physical risks to the sampler.
- **Compatibility**. The equipment must be chemically compatible with the material being sampled. For example, metal sampling tools may not be appropriate for sampling corrosive wastes or when testing for metals.
- **Representativeness**. The sampling equipment must allow for the collection of a representative sample.
- **Ease of Use**. Complicated sampling equipment is prone to operator error and breakdown.
- **Decontamination**. The ability to completely decontaminate sampling equipment in the field is another criterion important in equipment selection.

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5.2.1 SAMPLING SOLIDS

In many cases, solids are represented by a large volume of heterogeneous (non-uniform) materials. Characterization generally requires the collection of grab samples from numerous locations. To assist in sample location, a three dimensional grid in combination with random sampling may be used. If the waste is homogeneous (uniform), composite samples may be appropriate.

Following is a discussion of the basic equipment used to sample solids.

5.2.1.1 Augers

Augers can be used to sample solid material at varying depths and are commonly used to sample soil and large waste piles that cannot be sampled by other means. Augers are either hand-held or mounted on motor-driven hydraulic or mechanical units.

The hand-held unit of most versatility is the bucket auger (or soil recovery auger). For this unit, the auger blades cut a sample that is collected in a bucket or open cylinder immediately above the blades. The auger is removed when the bucket is filled and reinserted into the hole if a deeper sample is needed.

Sample collection from a standard auger is more difficult and less precise. The sample is collected by removing adhering material between the threads.

Hand-operated augers are useful only in solids that are free of rocks over 1 inch in diameter. To some extent, power driven augers can overcome the difficulty of rocky or consolidated materials. Both types of augers are generally unsuitable for dry loose solids. Additionally, all types of augers disturb the sample to varying degrees and cannot be used to collect discrete samples at a specified depth.

Hollow-stem augers solve the problem of sample disturbance. This type of motor-driven auger has a hollow center. The auger is inserted into the soil and then removed when maximum depth is reached. A thin-walled sampling tube is then driven in, essentially punching out an undisturbed sample. The thin-wall sampler may be constructed as a "split spoon." The sampler is split in two pieces along its length and held together on the top and bottom by screw rings. When the sampler is filled and extracted, the rings are removed and the two halves

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opened, thus exposing an undisturbed sample. Continuous samplers can also be used in conjunction with hollow-stem augers. In this case, a sample is pushed into a sampling tube at the same time the auger advances.

5.2.1.2 Core Samplers

A core sampler is used when consolidated materials are encountered that cannot be sampled by any other means and geologic characterization is required. The basic technique is similar to a hollow-stem auger, except that the auger is replaced by a bit capable of cutting through rock. Drilling fluids are used to cool and lubricate the bit. Thin-walled core samplers can be used to collect undisturbed vertical cores at desired locations.

5.2.1.3 Shovels and Scoops

Unconsolidated solids from piles, containers, and dumps can be collected by scoops and shovels. Scoops can be used when the solid waste is at or near the surface and is within easy reach of the sampler. Scoops come in a variety of sizes and are usually made of an inert material such as stainless steel or Teflon. Shovels can be used when larger quantities of sample are needed, when an extended reach is required, or when subsurface materials are to be collected. As with scoops, shovels are available in inert materials.

Both shovels and scoops have the same disadvantages. The worker collecting the sample must be near the sample being collected, thus increasing the risk of chemical exposure. In addition, collecting a representative sample with these sampling devices is difficult. Shovels and scoops generally collect a larger portion of the surface material than the subsurface. Overcoming this limitation is difficult, even when the sampler is aware of the problem.

5.2.1.4 Triers

A trier is useful in sampling loose, moist materials from waste piles, bags, and hoppers. The hand operated trier is inserted horizontally into the material being sampled and a core cut by rotating the instrument. A certain amount of moisture or stickiness is necessary to allow the material to hold together during removal. Triers are available in lengths from 61 to 100 cm and are usually made of stainless steel with a wooden handle.

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5.2.1.5 Thiefs

Thiefs consist or a long hollow outer tube with evenly spaced openings along its length. An inner tube with similar opening is oriented so that the openings are not aligned with the outer tube, and the entire dual-tube thief is inserted into the solid waste material. After insertion, the inner tube is rotated to align the openings, thus allowing the solid material to flow into the inner tube. The inner tube is then rotated back to the closed position, sealing the openings prior to withdrawal of the sampler. Thiefs can be inserted horizontally, vertically, or at various angles into the sample as long as the material will flow by gravity into the slots of the sampling tubes. This sampling device is best suited for sampling dry, free-running solids. It is available in a variety of diameters and is usually made of brass or stainless steel.

5.2.2 SAMPLING SLUDGES

Sludges contain a significant amount of liquid and range from dewatered solids to high viscosity liquids. Such materials are usually contained in drums, tanks, or impoundments, or are found in natural settings such as sediments in ponds or streams. Sampling commonly requires the use of extended-reach equipment to gain access to the submerged sludge layer.

Prior to sampling sludges, sampling objective must be reviewed to determine which fraction of the sludge will be analyzed. Sludge contains liquid and solid components. If both components are of interest, the sample must be taken in a manner that minimizes the loss of the liquid portion.

Following are some of the common equipment used to collect sludge samples.

5.2.2.1 Shovels and Scoops

These instruments can be used to collect sludge samples from shallow depth in drums, tanks, or surface impoundments. However, a significant portion of the liquid and finer solid fractions are lost when shovels and scoops are used, and the collection of a representative sample is usually difficult.

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5.2.2.2 Core and Auger Samplers

Both corers and augers can be modified to retain sludge samples. Core catchers, such as thin-walled tube samplers that prevent washout of the wet sludge during recovery of the sampler, are available for attachment to the tip of coring devices. Core catchers are available with extension sections that allow for collection of samples from depths well below the surface of the waste. The use of a core sampler equipped with a core catcher can provide for collection of profile samples. Sludges are deposited in layers over time, and the examination and sampling of this profile is often an important part of the sampling plan.

figure 1 hand held soil auger samplers

Bucket augers can also be used for sludge sampling. The bucket portion of the auger will collect liquids as well as solids. The bucket can be outfitted with a rubber flap on the top that will allow overlying liquids to flow through the auger when it is being inserted through the liquid, but will preserve sample integrity when the sample is pulled up.

5.2.2.3 Ponar Grab Sampler

This is a clamshell type scoop activated by a counter-lever system. The shell is opened and latched into place, then lowered to the bottom. A "messenger" or weight is then sent down the cable and trips the latching device and closes the clamshells.

The Ponar Grab Sampler is capable of collecting a variety of unconsolidated sludges. However, bottom weeds and rocks may prevent the device from closing and from collecting a sludge sample. In addition, the liquid portion is agitated and mixed with the overlying liquid, and this sampling device may not be useful for collecting the liquid of fine solid portion of the sludge.

5.2.2.4 Benthic Sampler

This simple device consists of a heavy brass cylinder with a sharpened bottom edge. A rubber flap is attached to the top to allow liquid transfer during descent and liquid retention during removal. The benthic sampler is allowed to free-fall to the bottom with the assumption that the weight of the device will be sufficient to drive the sampler to a reasonable depth into the sediment. The sampler is retrieved and contains both solid and liquid portions of the sediment.

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5.2.2.5 Glass Samplers

A glass tube or COLIWASA (discussed in Section 5.2.3.3) can be used to collect sludges from drums and shallow tanks. However, the glass sampler must be slowly inserted into the solid material, and this technique is applicable only for sludges easily penetrated by glass. When the glass tube is used, washout of the bottom portion of the sample is common, and this loss may represent a significant portion of the sludge sample. Use of the COLIWASA generally prevents washout.

figure 2 Sediment sampling tools

5.2.2.6 Sludge Sampler

This device consists of a heavy hollow cylinder with a pointed bottom and a lid on the top. The cylinder is attached to a pole. The weight of the sampler, usually about 30 pounds, allows the conical cylinder to penetrate into sludges. When the desired depth is reached, the top handle is lifted and rotated, thus opening the lid and allowing sludge to ooze into the cylinder. The handle is then turned to secure the lid over the cylinder and locked into position while the sample is removed from the sludge. Sludge samplers are generally made of stainless steel.

5.2.3 SAMPLING LIQUIDS

Hazardous waste liquids are commonly found in drums, tanks, impoundments, and ground water. The basic sampling equipment for these four categories is as follows.

- ! Drum sampling equipment includes dippers, a disposable glass tube or COLIWASA for full-depth sampling, or a pump with tubing that is lowered into the drum.
- ! Tanks require sampling equipment with extended reach capabilities. In addition, waste liquids in tanks are often stratified, and samples of each stratum may be needed. Tank sampling equipment includes a pump and tubing or discrete depth samplers such as subsurface grab samplers or Bacon Bomb samplers (described in Sections 5.2.3.5.2 and 5.2.3.5.3).
- ! Impoundment sampling presents a problem due to inherent hazards and poor accessibility. On-shore sampling is difficult unless a walkway or other structure extends over

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the impoundment. Off-shore sampling is somewhat easier but potentially dangerous. Access to offshore locations can be provided by floats, floating platforms, cranes with suspended enclosed platforms, and mobile boom vehicles with platforms. Impoundment sampling equipment usually includes dippers, subsurface grab samplers, Bacon Bomb samplers, discrete depth grab samplers, and AMS liquid samplers.

Following is a discussion of the more common tools used to sample liquids.

5.2.3.1 Dipper

A dipper is an open-ended container attached to a pole. Commonly, the dipper and pole are made of Teflon and the pole is capable of telescoping for an extended reach.

Dippers are suitable for collecting samples of the surface liquid layer in open drums and tanks, and in impoundments. This method is appropriate for wastes that are homogeneous and likely to be represented by a grab sample from the top layer. Additionally, dipper samples are useful if the subsurface layers are to be sampled by other means.

5.2.3.2 Glass Tube (Drum Thief)

A glass tube, 6 to 18 mm in diameter and generally 122 cm long, is inserted into a liquid, generally through the bung hole on a drum lid. The thumb is placed over the open end of the tube and a sample extracted. Generally, the glass tube is broken off against the drum lid and the contaminated tube remains in the drum for disposal.

The most serious limitation to tube samplers is spillage from the bottom of the tube. Such spillage is impossible to avoid, but can be minimized by using a smaller diameter tube.

This is the most common method of drum sampling because of its simplicity, low equipment cost, and minimal equipment decontamination.

5.2.3.3 COLIWASA

The COLIWASA (composite liquid waste sampler) is a large diameter borosilicate glass (or Teflon) tube with an inner rod attached to a ground glass seal at the bottom of the tube. The COLIWASA is inserted into the liquid with the inner rod elevated about one inch. When the sampler reaches the bottom, the inner rod is slowly lowered to seal the ground glass opening and a sample removed.

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The COLIWASA eliminates the problem of spillage inherent in a glass tube sampler. Unfortunately, this sampler is substantially more expensive than a glass tube.

5.2.3.4 Pumps

Pumps and associated tubing are useful for drawing liquid samples from a depth of approximately 8 meters. Peristaltic pumps are available in many sizes and flow rates to accommodate a variety of sampling situations. Full-depth composite samples can be collected by gradually lowering the tubing into the material being sampled. Pumps are usually run at a low flow rate to assist in minimizing the disturbance of liquid layers and to reduce agitation when the sample enters the sample bottle.

Submersible pumps can be used in some situations, but are limited by their inability to resist degradation by a variety of chemicals.

Most pumps introduce air into a liquid sample. This is undesirable if volatile organic compounds are to be analyzed. In addition, the introduced air can alter the chemical equilibrium of other constituents.

5.2.3.5 Discrete Depth Samplers

In many situations, liquids separate into layers and sampling must recover a particular layer or stratum. To accomplish this, discrete depth samplers are used. All of the devices listed below are designed to be manually opened or closed at a particular depth, thus recovering a sample of a particular stratum.

5.2.3.5.1 Kemmerer Sampler

This instrument is a spring-loaded cylinder that is lowered into a liquid in the open position to allow the liquid to flow through it while it is descending. At the desired depth, a messenger is dropped down the sample line, releasing a spring-loaded closing device thus obtaining a discrete depth liquid sample. Kemmerer samplers are usually constructed of brass and are difficult to decontaminate.

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5.2.3.5.2 Subsurface Grab Sampler

A one-liter sampling bottle is attached to a valve assembly; both units are then attached to a pole. The sampler is lowered to the desired depth and a cable pulled. The cable opens the valve and the bottle fills. A modular design on the pole allows for the attachment of six foot sections up to a total length of 30 feet.

These discrete depth grab samplers are made of glass for the sampling container, stainless steel or Teflon for the pole, and polypropylene or teflon for the head.

5.2.3.5.3 Bacon Bomb Sampler

This sampling device is lowered on a sample line. A second line attached to an opening rod (this rod runs down the center of the bomb) opens the sampler when pulled. A discrete-depth sample can be collected with a minimal amount of agitation since the rod can open the top and bottom of the bomb, allowing the sample to enter the bottom and air to exit through the top. Unlike the Kemmerer Sampler, the Bacon Bomb sampler can be lowered to the desired depth in the closed position before collecting a sample, thus minimizing cross-contamination.

Discrete depth samplers are made of brass, Teflon, or stainless steel. They require careful maintenance and regular inspection for proper functioning.

5.2.3.5.4 AMS Liquid Sampler

This stainless steel and Teflon sampler is designed to obtain a discrete sample at a specified depth or a composite sample from several intervals throughout the substance. It is similar to a Bacon Bomb sampler in that it fills from the bottom of the sampling container. A sample is collected by lifting the hand level that opens a ball check valve on the sampler. Samples can be collected to a 25-foot depth.

5.2.3.6 Bailers

A bailer consists of a cylinder with a ball check valve in the bottom and an open top with a cable or rope attachment. When the bailer is lowered into the water column, the force of the water pushes the ball upward and water flows into and out of the bailer. When the bailer is pulled upward, the ball seats in the opening and prevents water from exiting. This column of water is then removed from the well. Some bailers have a tripping mechanism that allows it to fill at a specific depth when a discrete depth sample is needed.

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Reusable bailers are usually made of stainless steel or Teflon; disposal bailers are made of various plastic resins. The cables or ropes attachment is can be made of a variety of materials, and selection is dependent on analytical parameters, decontamination, and cost.

5.2.4 SAMPLING BULK MATERIALS

Bulk materials are often a relatively homogenous collection of a single identifiable product. These materials are generally containerized, although the material may be pile directly on the ground. The heterogeneity present within an exposed pile can be predicted based upon the degree of surface exposure to the atmosphere and/or background information on the manufacturing or sources of the material. Thus, one must consider that there can be changes in composition with respect to time (degree of exposure to the atmosphere or degree of "maturation") and with respect to distance (changes in the composition across the cross-section of the pile). This requires collecting grab samples which will characterize this structured heterogeneity. Generally the sampling approach will include representative sampling of the outer surface zone and then the interior portions of the pile. A coring device would facilitate this type of sampling. If there is no reason to expect such heterogeneity, then it is common to composite a number of grab samples in order to increase the representativeness of the analyzed sample and reduce analytical costs. A composite sampling approach should be pre-planned to insure that the resulting data is meaningful.

Bulk materials in an unconsolidated state may be readily collected by a stainless steel/polyethylene scoop, a coring device with a sample catcher at the end, a trier or a grain thief. The grain thief is limited to unconsolidated materials which possess particle sizes smaller than the openings. A grain thief consists of a long hollow tube with evenly spaced openings along its length. The tube openings are initially in a closed position via an outer sleeve as the thief is inserted into the pile. Upon complete insertion, the inner sleeve is rotated until its openings align with those on the outer sleeve. The bulk material then enters the device, the inner sleeve is rotated to a sealed position, and the device is withdrawn.

5.2.5 Sampling Artifacts

Attempting to characterize potential contamination of artifactual materials, such as a wall within a building or a counter-top, can be quite

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challenging. Obtaining a representative cross-sectional sample from a wall or a monolithic structure would require using a powered coring device. Such activity requires careful planning to ensure sample integrity and that the operation was completed in a safe manner. reduction of the sample for laboratory analysis is very challenging, especially for VOAs. The results of TCLP analysis will vary greatly depending on the degree to which particle size reduction is employed.

Determination os surface contamination can be completed easily using a variety of field screening instruments and/or by completing a wipe sample. Wipe sampling is also used to ascertain whether equipment decontamination has been effective. Generally, wipe sampling entails rubbing a moistened filter paper over a measured area of 100 cm^2 to 1 m^2 and the paper is then sent to the laboratory for analysis. It is important to quantify the exact surface are wiped as the analytical results must be related to the known area of the sample. The sampler should use a clean, impervious disposable surgeon's glove for each sampling. The filter is moistened with a solvent which will dissolve the contaminants of concern. Typical solvents include distilled, deionized water or the solvent used in the lab analysis.

5.3 DECONTAMINATION

Sampling equipment must be decontaminated between each sample to protect against cross contamination. Decontamination usually consists of a water-based solution (such as soap and water) followed by a rinse solution (generally water). Decontamination solutions are based on the characteristics of the chemicals to be removed from the equipment. Solutions are often dispensed in a pressurized portable tank, such as those commonly used to apply yard pesticides.

All decontamination solutions must be collected and treated as hazardous waste. In most cases, the solutions are collected in a drum and left on-site.

In addition to equipment decontamination, worker decontamination is necessary. Glove decontamination is especially important in that gloved hands generally contact the material being sampled. Other protective equipment may also require decontamination.

5.4 SAMPLING CONTAINERS

A variety of factors affect the selection of sampling containers. Size, material compatibility, and lid type are among the more important factors.

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5.4.1 CONTAINER SIZE

Laboratory analysis requires a certain sample volume or weight for analysis. Therefore, a container of the appropriate size must be selected. Container sizes generally range from 20 to 1000 ml.

5.4.2 MATERIAL COMPATIBILITY

The sample must be compatible with the container; any type of sample-container reaction will destroy the integrity of the sample. General compatibility rules are as follows:

- glass is usually required when samples are to be analyzed for organics;
- plastic or glass can be used when samples are to be analyzed for metals;
- plastic should be used when samples are to be analyzed for boron or silica;
- amber glass should be use when samples are photosensitive;
- special VOA vials must be used when volatile organics in water are to be analyzed;
- glass should be used for solids and sludges requiring pH analysis; and
- glass is required for analysis of oil, grease, and phenolics.

5.4.3 LIDS

Lids are part of the sample container and must be considered, especially in terms of compatibility. The interior of the lid must be compatible with the sample and the analytical parameters. Most lids are lined with either Teflon or aluminum foil. In addition, some lids are specially designed with a Teflon insert (or septum) that allows analytical access to the sample without removing the cap.

Lids are available in either narrow or wide mouth forms. Narrow mouth lids are generally used for liquids because of less likelihood for leakage. Wide mouth lids are generally used for sludges and solids.

5.4.4 CONTAMINATION

Sampling containers should be used as received (generally from the lab). For example, containers should not be rinsed out prior to use.

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This may remove preservatives that have been placed in the container. In addition, rinsing invites contamination.

Tape should not be used on containers. Most tapes have organic glues that can penetrate the container cap and contaminate the sample.

Contamination is also minimized by not opening the sample container until immediately prior to sample collection and by closing the container immediately after sample collection.

5.5 LABELS

All sampling containers must have labels. Labels are generally supplied by the laboratory and require a variety of information including company, project, sample identification such as location or number, sampler, date and time sampled, sample type (raw or filtered), and preservatives.

Information required on the label should be written in prior to sample collection. Sample collection may result in a wet or dirty label that repels ink. The information on the label should agree with all entry on other forms, such as the chain-of-custody form and sample log sheet.

Most labels are of the self-adhesive type. They should be applied to the sample container prior to sample collection. Labels do not stick well to wet or dirty containers.

5.6 SAMPLE PRESERVATION

The objective of sample preservation is to ensure that the chemical characteristics of the sample do not change from the time of collection to the time of analysis. Preservation techniques depend on the analytical parameters, and in most cases, the analytical laboratory will specify the required sample preservation. Common presentation techniques are as follows.

- **Low Temperature**. Immediately cooling samples to 4 degrees Centigrade is the basic sample preservation technique. This is implemented by using coolers and packaged coolants. Samples should not be allowed to freeze.

- **Acid Preservation**. Liquid samples can be preserved by adding acid, usually nitric, sulfuric, or hydrochloric, to lower the pH to less than 2.

- **Basic Preservation**. Liquid samples can be preserved by

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adding bases, such as sodium hydroxide, to increase the pH to greater than 9.

! **Filtering**. Water samples that require analysis for dissolved metals must be field filtered.

! **Zinc Acetate**. Some analytical parameters, such as sulfides, require a zinc acetate preservative.

Other preservation techniques include storage in a dark area (usually in a cooler), use of amber glass, and the elimination of head space in the filled container.

In most cases, the analytical laboratory will place the appropriate preservative in the sample containers prior to shipping the containers to the field. In addition, laboratories also supply coolers, packing material, cold packs, labels, chain-of-custody forms, etc.

Once a sample has been properly preserved, it has a shelf life or holding time. Holding times range from zero (such as pH for a liquid) to months. Regardless of the holding time, samples should be transported to the laboratory immediately after collection. The laboratory then retains the sample for the appropriate period of time. Sample retention and holding times are critical when sample analysis is phased (second tier analysis depends on the results from the first tier).

5.7 SHIIPPING

Prior to transporting samples to the laboratory, the containers must be properly packed to prevent breakage. Plastic bubble pack, styrofoam, or vermiculite are commonly used for cushioning. Vermiculite is probably the best packing material because is not only cushions but it absorbs any spilled liquid. However, this material is messy during unpacking, and some laboratories will not accept vermiculite.

Samples are normally packed in coolers. Custody seals, packing slips, chain-of custody forms, and other documents must accompany the shipment. In addition, shipping certain quantities of particular substances may require DOT labels and shipping procedures.

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5.8 CHAIN-OF-CUSTODY

Because samples collected during a site assessment may be used as evidence in court, possession must be traceable from the time the samples are collected until the data are introduced as evidence during legal proceedings. To maintain and document sample possession, chain-of-custody procedures are followed. The chain-of-custody form documents possession. The EPA defines possession (or custody) as follows:

- physical possession of samples;
- previous physical possession and now samples are in sight;
- previous physical possession and samples have been placed in a secure area (including a shipper); and
- previous physical possession and samples are now in a locked container.

Therefore, the field sampler is personally responsible for the care and custody of the samples collected until they are properly transferred to another person who accepts custody. Whenever

table 1
table 2
figure 3 examples of labels

possession changes, the chain-of-custody form (Figure 4) must be signed and dated by the person relinquishing custody and the new person accepting custody.

The chain-of-custody form is wrapped in a plastic bag and placed inside the sample cooler. In addition, custody seals are usually placed over the lid of the cooler in such a manner that they are torn when the cooler lid is opened.

The chain-of-custody also serves as a sample log sheet where sample description and analytical parameters are specified. As shown in Figure 1, a variety of other information may be required on this form.

5.9 INTERFACING WITH THE LABORATORY

The analytical laboratory is an integral part of every sampling program. Laboratory personnel should be involved prior to, during, and after sampling. All too often, the laboratory is forgotten until they receive the sample and cannot complete the required analysis because of some mistake or misunderstanding on the part of the sampler. Following is a brief review of the role of the laboratory in a site assessment.

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5.9.1 SELECTION OF A LABORATORY

Although price is usually the most important criterion in selecting a laboratory for sample analysis, other factors should be considered. Some of these factors are as follows:

- ! certain analyses, such as drinking water, require state certification;
- ! CERCLA samples must be analyzed by a laboratory within the EPA contract lab program;
- ! adequate quality assurance/quality control plan; and
- ! adequate number of control samples.

5.9.2 CONTAINERS

The laboratory usually supplies the sampling containers. Items such as material, size and number of containers, labeling, preservation, coolers, cooling material, packing material, chain-of-

figure 4 an example of a chain-of-custody form

custody forms, labels, etc. must be specified if the laboratory is to function as intended.

5.9.3 METHOD OF ANALYSIS

Analytical methods depend on what is under investigation, why the investigation is taking place, and the regulatory agency. In many cases the EPA has specified methods of analysis for projects under their jurisdiction. However, methods change, so both the sampler and the laboratory must be aware of changes to ensure that the proper methods are used. Detection limits must be set and are based on the needs of the project and the capabilities of the analytical equipment.

If the analytical program is phased, description of each phase, criteria limits and other details must be coordinated with the sampler and the laboratory.

5.9.4 ANALYTICAL QUALITY

Methods of laboratory quality control and quality assurance should be examined to ensure that project standards can be met. Details of this program for both the field and laboratory are discussed in the next

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section.

5.9.5 DATES

As previously discussed, sample holding times are very important, especially when phased analysis is conducted. Coordination between sampler and laboratory is essential to prevent analytical voids due to expired holding times.

Turn-around time is also important and is probably the most common source of misunderstanding between the sampler and the laboratory.

Delivery dates and times must likewise be specified. Someone must be at the laboratory to accept sample custody and to unpack and log in the samples as soon as they arrive. After hours or weekend sample deliveries must be coordinated with the laboratory.

5.9.6 LABORATORY SAFETY

Samplers are obligated to specify expected concentrations in sample parameters. This allows the laboratory to properly set their instruments, thus avoiding costly delays and repeated analyses. In addition, highly concentrated samples can pose a hazard to laboratory personnel and can contaminate the laboratory. This is especially important when samples of pure product, such as pesticide, are sent for analysis.

Disposal of excess sample material must be addressed. Most laboratories are large quantity hazardous waste generators and operate under RCRA regulations. Laboratories can drum samples and ship them to an incinerator, or send them back to the sampler for proper disposal.

5.10 QUALITY ASSURANCE/QUALITY CONTROL

Quality assurance and quality control (QA/QC) is a management program to ensure that the specified standards of quality are maintained throughout the sampling and analytical program. The QA/QC plan usually contains such items as project description, sampling procedures, sample custody, equipment calibration, analytical procedures, data reduction, quality control checks, performance audits, precision, accuracy, control samples, and reporting. A few of these items are discussed in more detail below.

5.10.1 ACCURACY AND PRECISION

Accuracy is a measure of how close the analytical values are to the real value. In contrast, precision measures the ability to duplicate

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results. Both accuracy and precision are necessary in a QA/QC program.

5.10.2 QUALITY CONTROL SAMPLES

A variety of quality control samples may be collected in the field to assist QA/QC evaluation both in the field and in the laboratory. These samples are as follows.

- **Field Duplicate, Replicate, or Split** CTo measure analytical precision, duplicate samples are taken of the same media, being careful that one sample is the twin of the other. With respect to the laboratory, field duplicates are usually "blind;" in other words, the laboratory does not know the sample is a duplicate. In some cases, sample splits must be offered to the facility owner. The owner may have the samples analyzed by another lab, thus determining analytical precision between labs. For some analyses (such as volatile organics and trihalomethanes), duplicates are required. If the collected samples is non-homogeneous (such a soil), then the sample must be homogenized (except for VOA samples) and split in a representative manner.

- Field SpikeCa duplicate sample is collected, but to one sample a known amount of a chemical (analyte) is added. This is used to determine analytical accuracy. However, an exact amount of a particular analyte to accomplish in the field. Additionally, this does not fully take into account "matrix," or the mass that encloses the sample. Field spikes are rarely used.

- **Field Method Blank**Cfollowing routine equipment decontamination, the process is repeated and decontamination solution collected for analysis. A sample of unused decontamination solution is also collected. A comparison of the analytical results will determine the effectiveness of field decontamination.

- **Field Blank**Ca sampling container is filled with distilled water at the same time a sample is taken. This is commonly used if air-borne contaminants are of concern. This is sometimes called an ambient blank.

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- **Field Preservation Blank**Ca sampling container is filled with distilled water and a preservative added. This will determine if any contamination is introduced by the preservative.

- **Rinseate Blank**Cdistilled or "laboratory grade" water is flushed through a sampling instrument and the rinseate is then sent to the lab for analysis. This type of blank can be collected prior to sampling or following sampling and decontamination. Collecting a rinseate sample is an effective means of demonstrating contamination-free sampling equipment. This is also referred to as an "equipment blank."

- **Trip Blank**Cthe laboratory fills a container with distilled water and sends it with the other sampling containers. This quality control sample is not opened in the field, but is other wise treated the same as other samples. Analysis of this sample will determine any contamination takes place from the time containers leave the laboratory until they return. Contamination may occur when containers are prepared in the lab if samples are not properly capped, improperly cleaned cooler, in appropriate packing material, etc. Trip blanks are required for certain analyses such as volatile organics.

Material blanks may be collected during some sampling programs. These are samples of construction materials, such as the sand or grout used when installing a ground water well, that may introduce contaminants.

There is considerable debate regarding the nomenclature and types of quality control samples that are taken in the field. Therefore, for a given sampling effort, the above definitions may change slightly.

The frequency of quality control sample collection must be clearly communicated and documented prior to sampling activities. Types and frequency of quality control sample collection are generally specified by the applicable regulatory agency.

In addition to these field control samples, the laboratory has internal quality controls. These controls usually consist of a method blank (distilled water or solvent), and blank spikes (a method blank plus a known amount of analyte) and matrix spikes for determination of accuracy; and matrix spike duplicates and sample duplicates to determine precision. Also, calibration standards are used to help insure instrumental accuracy and precision.

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5.11 DATA INTERPRETATION

Once laboratory data has been received, a determination must be made on whether the material sampled is a hazardous waste. The two areas of data needs which are followed by interpretation include:

- Waste Characterization
- Chemical Composition and Concentration

5.11.1 WASTE CHARACTERISTICS

Certain RCRA requirements require a determination of whether a material is solid or liquid. For example, the flashpoint test for ignitability, and the characteristic of corrosivity apply only to liquids. If the physical state (i.e., solid or liquid) of the sample is in question, the data must note whether the material passes EPA Method 9095, the Paint Filter Liquids Test contained in EPA Publication No. SW-846 (see Section 260.11(a)).

The data must also indicate the sample's status under the four characteristics set forth in Section 260.20 to 260.24. For example, the data must be compared against the standards for corrosivity by determining:

- Does the liquid have a flashpoint less than 140 ^{o}F (261.21(a)(1))
- Does the non-liquid substance, under standard temperature and pressure, cause fire through friction, moisture absorption, or spontaneous chemical changes? (261.21(a)(2))
- If it is a gas, does it meet the standards for compressed gas set forth in 49 CFR 173.300? (261.21(a)(3))
- Does it meet the standards for an oxidizer set forth in 49 CFR 173.151 (261.21(a)(4))

Unless the generator can exclude the possibility of a waste being hazardous through knowledge of the materials or processes used to generate the waste, it must ensure that the data demonstrates the waste is nonhazardous for <u>all</u> characteristics, from D001 (ignitability) through D043 (TCLP for vinyl chloride).

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The toxicity characteristic (261.24, Waste Code D004-D043) requires particular attention, since the generator must determine both what the sample extract contains (are one of the forty TCLP contaminants present, and how much of the listed contaminant (above or below the regulatory level) it contains.

5.11.2 CHEMICAL COMPOSITION

The chemical composition of a waste is needed to determine if that mixture of waste is a listed waste or if it meets the land disposal restrictions treatment levels.

Determining whether a waste is listed involves a different type of data interpretation. Specific source K wastes require no data interpretation, since that listing depends on the industrial process which created the waste, not the chemical composition of the waste.

Non-specific source F waste listing also depends on the process which created the waste, not its ultimate chemical composition. However, it is critical to determine the composition of solvent F wastes (F001-F005) prior to their use as solvents. For example, the spent halogenated degreasing solvents listed at F001 are hazardous wastes only if they made up at least 10% of the solvent prior to use.

U and P waste listing applies only to pure, unused chemical products. Laboratory analysis of these products would be required only when a substance is unknown, such as when an inventory turns up an unlabelled drum full of white powder. In that case, the lab data must be compared against the lists set forth in 261.33 (acutely hazardous P wastes) and 261.34 (hazardous U wastes). In most other cases, the chemical can be identified from its marking, labelling, or from company inventory records.

5.11.3 LAND DISPOSAL RESTRICTED WASTE

Hazardous wastes are not excluded from land disposal if they meet the EPA's treatment standards. The treatment standards are designed to reduce the toxicity or the mobility of the waste constituents. therefore, it is helpful to view the LDRs not as a complete ban on the land disposal of waste, but as a pretreatment requirement which must be met before land disposal.

The EPA has issued treatment standards for all restricted wastes. These treatment standards are expressed as:

! Constituent Concentration in Waste Extract (CCWE) - The CCWE is found in 40 CFR 268.41.
! Constituent Concentration in Waste (CCW) - The CCW is

found in 40 CFR 268.43.

- Technology-Based Standards by RCRA Hazardous Waste Code -The Technology Based Standards are found in 40 CFR 268.42.
- Technology Based Standards for Specific Radioactive Hazardous Mixed Waste - The Technology Based Standards for Specific Radioactive Hazardous Mixed Waste are found in 40 CFR 268.42.

Data from the laboratory must be evaluated and interpreted for compliance with these LDR treatment standards. Since a waste can appear on more than one treatment table, it is critical that a person managing hazardous waste carefully examine each table of the treatment standards before determining the treatment method for each waste.

For example, D009 mercury-containing wastes must be reviewed for compliance with CCW, CCWE, and Technology-based standards, in addition to the TCLP toxicity standards. F005 wastes are also subject to three LDR pretreatment standards. The generator must ensure that when the laboratory demonstrates that a substance is a hazardous waste, it also runs any required tests to determine LDR compliance. The LDR test may have to be performed on the sample itself, for that waste's LDR constituents, or on the sample extract, for CCWE constituents.

For a more complete discussion of the LDR's including the spent solvent rule, dioxin rule, California wastes, and the first, second and third wastes see Unit 2 of this training manual.

5.12 ADDITIONAL READING

Environmental Protection Agency. 1984. Characterization of Hazardous Waste Sites-A Methods Manual: Vol. II. Available Sampling Methods. EPA/600/4-84-076.

Environmental Protection Agency. 1987. A Compendium of Superfund Field Operation Methods. EPA/540/P-87/001.

Environmental Protection Agency. 1992. Characterizing Heterogeneous Wastes: Methods and Recommendations. EPA/600/R-92/033.

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EPA. 1984. A Soil Sampling Quality Assurance User's Guide. EPA 600/4-85-043.

EPA. 1985. Sediment Sampling Quality Assurance User's Guide. EPA 600/4-85-048.

EPA. 1987. A compendium of Superfund field operations methods. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response. EPA 540 p. 87.001.

EPA. 1989. Interim final RCRA facility investigation (RFI) guidance. U.S. Environmental Protection Agency, Waste Management Division Office of Solid Waste. EPA 530/SW-89-031.

Keith, lL. H. 1988. Principles of environmental sampling. American Chemical Society, Salem, MA.

O'Brien & Gere Engineers, Inc. 1988. Hazardous waste site remediation, the engineer's perspective. Van Nostrand Reinhold, New York.

TABLE 1{PRIVATE }
SAMPLE CONTAINERS, SAMPLE PRESERVATION,
AND SAMPLE HOLDING TIMES FOR SOLIDS SAMPLES

{PRIVATE }Parameter	Container	Preservative	Holding Time
Soil or Sediment Samples - Low to Medium Concentration			
Organic Compounds:			
Purgeable Organics (VOCs)	1 x 4-oz wide mouth teflon-lined glass vials	Cool, 4^{o}C	7 days
Extractable Organics (BNAs), Pesticides and PCBs	1 x 8-oz wide-mouth teflon-lined glass vials	Cool, 4^{o}C	7 days until extraction, 40 days after extraction
Inorganic Compounds:			
Metals (TAL)	1 x 8-oz wide-mouth glass jar	Cool, 4^{o}C	180 days[1]
Cyanide	1 x 8-oz wide-mouth glass jar	Cool, 4^{o}C	28 days
Sulfide	1 x 8-oz wide-mouth glass jar	Cool, 4^{o}C	14 days
Nitrate	1 x 8-oz wide-mouth glass jar	Cool, 4^{o}C	28 days
Radionuclides	1 x 1-l wide-mouth glass jar	None	45 days

[1]Holding time for mercury is 28 days.

TABLE 2

FIELD QC SAMPLE FREQUENCY

Sample Type	Type of Analysis	Media Solids	Media Liquids
Duplicates	Organics	1/10	1/10
	Inorganics	1/10	1/10
	Radionuclides	1/10	1/10
Field Preservation Blanks	Organics	NA	NA
	Inorganics	NA	1/20
	Radionuclides	NA	1/20
Equipment Rinsate Blanks	Organics	1/20	1/20
	Inorganics	1/20	1/20
	Radionuclides	1/20	1/20
Trip Blanks	Organics (Volatiles)	NR	1/20
	Inorganics	NR	NR
	Radionuclides	NR	NR

NA = Not Applicable
NR = Not Required